

UNITED STATES PATENT APPLICATION

of

KARL J. URQUHART

JOE G. HOFFMAN

DAVID SNYDER

VINOD RAGHAVAN

MARY D. HAVLICEK

and

JOHN GEURIAN

for

CHEMICAL PURIFICATION CARTRIDGE

Attorney Docket No.: 016499-706  
BURNS, DOANE, SWECKER & MATHIS, L.L.P.  
POST OFFICE BOX 1404  
ALEXANDRIA, VIRGINIA 22313-1404  
(703) 836-6620

## CHEMICAL PURIFICATION CARTRIDGE

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

[0001] The present invention relates to cartridges and apparatuses for purifying a liquid chemical. The present invention also relates to methods for purifying a liquid chemical. The invention has particular applicability in the semiconductor manufacturing industry.

#### 2. Description of the Related Art

[0002] In the semiconductor manufacturing industry, a major concern at every stage in the manufacturing process is contamination. Control of contamination is important to product quality, and an extremely high level of cleanliness and purity in the manufacturing environment is typically required to obtain acceptable product yield while maintaining profitability. Accordingly, many of the steps in modern integrated circuit (IC) manufacturing are dedicated to cleaning the semiconductor wafers being treated. Such cleanup steps are implemented to remove, for example, organic contaminants, metallic contaminants, photoresist (or inorganic residues thereof), byproducts of etching and native oxides.

[0003] A significant source of contamination is the process chemicals themselves, which contain various impurities. Process chemicals are frequently used in the cleanup steps of the manufacturing process which help maintain product quality. Contamination present in such process chemicals is undesirable.

[0004] In wet processing steps, a liquid reagent can be used for a variety of purposes including, for example, the etching of silicon dioxide, silicon nitride or silicon. The liquid reagent can also be used for removing native oxide layers, organic materials, trace organic/inorganic contaminants or metals. The purity of the liquid chemicals typically affects the yield and the reliability of the devices being formed. In liquid cleanup steps that are directly followed by high-temperature processes, contaminants on the wafer surface are typically driven and/or diffused into the wafer.

[0005] A major concern for wet process chemicals is ionic contamination. IC devices generally include only a few dopant species such as, for example, boron, arsenic, phosphorus and antimony, to form the p-type and n-type doped regions of the devices. However, contaminants present in the chemicals used in wet processing steps can also act as electrically active dopants and have deleterious effects on the IC devices. Thus, the presence of these contaminants is highly undesirable.

[0006] It is therefore apparent that liquid chemicals for treating semiconductor wafers should have extremely low concentrations of impurities including, for example, metal ions. Preferably, the total metal content should be less than 300 ppt (parts per trillion), and preferably less than 10 ppt for any single metal.

[0007] Hydrogen peroxide ( $H_2O_2$ ) is commonly used in wet cleanup process steps in the manufacturing of a semiconductor wafer. For example, the widely used "piranha" cleanup solution typically includes hydrogen peroxide and sulfuric acid ( $H_2SO_4$ ) in a ratio of about 30:70. In addition, the widely used "RCA" cleanup procedure typically has three-stages, two of which can include the use of hydrogen peroxide.

[0008] Hydrogen peroxide is generally not easily purified. For example, the decomposition of hydrogen peroxide can be exothermic, temperature sensitive, and/or catalyzed by various contaminants. Hydrogen peroxide is also a powerful oxidant. In addition, certain materials used to purify hydrogen peroxide can also contribute to its decomposition.

[0009] Conventional columns that are used for purifying hydrogen peroxide typically present safety concerns. For example, contacting hydrogen peroxide with a purification material, such as an ion exchange bed, to remove ionic contaminants therefrom can evolve oxygen. The generation of oxygen typically results in the accumulation of pressure. Conventional columns containing a purification material are typically made of rigid and inflexible material. Such material is typically unable to expand, tear or otherwise compensate for the accumulating internal pressure. If not properly maintained, such columns can explode when under excessive amounts of pressure, resulting in equipment damage

and constituting a safety hazard. Thus, careful monitoring of the pressure within the column is typically required.

[0010] Conventional hydrogen peroxide purification columns typically are periodically shut down for maintenance purposes. The replacement of the purification material inside a column generally requires the column to be shut down, for example, for about two days. This decreases the productivity of the column. Furthermore, the conventional column typically employs gravity flow of the chemical therethrough, thereby requiring the column to be positioned vertically. This can place limits on where the column can be installed. The use of gravity flow can also limit the flow rate of the chemical through the column, for example, to less than 1 lpm (liter per minute).

[0011] The flow characteristics of the hydrogen peroxide through the purification material provided by current purification columns can present additional disadvantages. For example, the flow characteristics can cause sulfates, nitrates and/or chlorides present in the purification material to be released into the hydrogen peroxide, thereby contaminating the purified product. For example, hydrogen peroxide purified by a current column typically contains from about 15 to 22 ppb of each of sulfates, nitrates and/or chlorides. The flow characteristics can also cause prolonged contact between the hydrogen peroxide and the purification material, which in turn can produce an excessive amount of oxygen gas. As discussed above, the production of oxygen gas typically generates pressure within

the column and can cause equipment damage and present a safety hazard.

[0012] Current on-site chemical purification systems are typically expensive. For example, the equipment used in such systems can cost upwards of one million dollars. Maintenance of the equipment can incur additional costs. Further, the equipment typically occupies a relatively large space, thereby limiting the usable area in a semiconductor manufacturing facility.

[0013] Consequently, to meet the requirements of the semiconductor processing industry and to overcome the disadvantages of the related art, it is an object of the present invention to provide cartridges, apparatuses and methods for purifying a liquid chemical that can conspicuously ameliorate or eliminate the above-described disadvantages of the related art.

[0014] Other objects and aspects of the present invention will become apparent to one of ordinary skill in the art upon review of the specification, drawings and claims appended hereto.

#### SUMMARY OF THE INVENTION

[0015] The foregoing objectives are met by the present invention. According to a first aspect of the present invention, a cartridge for purifying a liquid chemical is provided. The cartridge includes:

- [0016] (a) a conduit connected to receive a flow of a chemical to be purified; and
- [0017] (b) a packed section in the conduit comprising a purification material, wherein the ratio of the length of the packed section to the inside diameter of the conduit is from about 8:1 to about 200:1, and wherein the flow of the chemical to be purified contacts the purification material, thereby producing a flow of a purified chemical.

[0018] According to another aspect of the present invention, a method for purifying a liquid chemical is provided. The method includes introducing the flow of the chemical to be purified to the cartridge described above.

[0019] According to another aspect of the present invention, an apparatus for purifying a liquid chemical is provided. The apparatus includes:

- [0020] (a) a chemical source for providing a main flow of the chemical to be purified; and
- [0021] (b) a plurality of the cartridges described above, wherein the plurality of the cartridges is connected to receive the main flow of the chemical to be purified.

[0022] According to another aspect of the present invention, a method for purifying a liquid chemical is provided. The method includes introducing the main flow of

the chemical to be purified to the plurality of the cartridges of the apparatus described above.

[0023] According to a further aspect of the present invention, a detachable fitting for connection to a fluid transport line is provided. The fitting includes:

[0024] (a) a conduit having an inlet end for receiving a flow of fluid from a fluid-providing line and an outlet end for introducing the flow of fluid to a fluid-receiving line;

[0025] (b) a first connection device arranged to removably connect the inlet end of the conduit to the fluid-providing line;

[0026] (c) a second connection device arranged to removably connect the outlet end of the conduit to the fluid-receiving line; and

[0027] (d) a device disposed inside the conduit, wherein the flow of fluid contacts the device.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0028] The objects and advantages of the invention will become apparent from the following detailed description of the preferred embodiments thereof, in connection with the accompanying drawings, in which like features are designated by like reference numerals, and in which:

[0029] FIG. 1A illustrates a side view of an exemplary cartridge for purifying a liquid chemical, according to one aspect of the invention;



[0030] FIG. 1B illustrates a side view of an end member of the exemplary cartridge shown in FIG. 1A, according to another aspect of the invention;

[0031] FIG. 1C illustrates an exploded side view of an end member of the exemplary cartridge shown in FIG. 1A, according to another aspect of the invention;

[0032] FIG. 2 illustrates a block flow diagram of an exemplary apparatus for purifying a liquid chemical, according to another aspect of the invention;

[0033] FIG. 3 illustrates a block flow diagram of an exemplary apparatus for purifying a liquid chemical according to another aspect of the invention, wherein the apparatus is connected to receive a chemical to be purified from a mobile source;

[0034] FIG. 4 illustrates a block flow diagram of an exemplary apparatus for purifying a liquid chemical according to another aspect of the invention, wherein the apparatus is connected to receive a liquid chemical to be purified from a mobile source and to pass a purified chemical to a day tank;

[0035] FIG. 5 illustrates a block flow diagram of an exemplary apparatus for purifying a liquid chemical according to another aspect of the invention, wherein the apparatus is connected to receive a liquid chemical to be

purified from a chemical dispensing unit (CDU) and to pass a purified chemical to various points of use; and

[0036] FIG. 6 illustrates a block flow diagram of an exemplary apparatus for purifying a liquid chemical according to a further aspect of the invention, wherein the apparatus is connected to receive a liquid chemical to be purified from a bulk storage tank and to store a purified chemical in a plurality of storage tanks.

DETAILED DESCRIPTION OF THE  
PREFERRED EMBODIMENTS OF THE INVENTION

[0037] The invention will now be described with reference to FIG. 1A, which illustrates a cartridge 100 in accordance with an exemplary aspect of the present invention. The cartridge 100 purifies a liquid chemical. The cartridge 100 can generate a flow therethrough having flow characteristics which are effective for increasing the purity level of the chemical passed therethrough. The purified liquid chemical is preferably suitable for use in a semiconductor fabrication process.

[0038] The liquid chemical to be purified can be any chemical that is capable of being purified through contact with a purification material. For example, the chemical to be purified can be a hydrogen peroxide solution, hydrofluoric acid, hydrochloric acid, ammonium hydroxide solution, acetone, isopropyl alcohol or water. Combinations of chemicals can also be purified such as, for example, mixtures of acetic and hydrofluoric acid, ammonium hydroxide

and hydrogen peroxide, or hydrochloric acid and hydrogen peroxide. Other chemicals and chemical mixtures used in the semiconductor fabrication industry can also be purified.

[0039] In a preferred embodiment, the chemical to be purified comprises a hydrogen peroxide solution. For example, given a hydrogen peroxide feed solution containing from about 1 to about 10 ppb metallic impurities per contaminant and from about 20 to about 30 ppm total organic carbon impurities, the cartridge 100 can typically provide a purified hydrogen peroxide solution having a cationic concentration of less than or equal to about 1 ppb per cationic contaminant, an anionic concentration of less than or equal to about 10 ppb per anionic contaminant, and a total organic carbon contaminant concentration of less than or equal to about 20 ppm.

[0040] The cartridge 100 includes a conduit 104 having an inlet 102 and an outlet 106. The inlet 102 is connected to receive a flow of the chemical to be purified. The flow of the chemical to be purified flows through the conduit 104. The conduit 104 is partially or entirely packed with a purification material 105, preferably entirely packed with the purification material 105. The purification material 105 disposed in the conduit 104 forms a packed section 107 of the conduit 104. The density of the packed purification material 105 will depend, for example, on the type of purification material employed. The flow of the chemical to be purified contacts the purification material 105 disposed in the conduit 104, thereby producing a flow of a purified

chemical. The flow of the purified chemical is removed from the conduit 104 via the outlet 106.

[0041] The dimensions of the cartridge 100 can depend on several factors including, for example, the desired flow rate of the chemical through the cartridge 100, the characteristics of the chemical to be purified and/or the characteristics of the purification material 105 that is employed. The dimensions of the cartridge 100 should be sufficient to accommodate the packed section 107 of the conduit 104. The ratio of the length of the packed section 107 of the conduit 104 to the inside diameter of the conduit 104 is typically from about 8:1 to about 200:1, preferably from about 15:1 to about 50:1, and more preferably about 25:1. The inside diameter of the conduit 104 is typically from about 0.25 to about 2 inches (about 0.64 to about 5.08 cm), preferably from about 0.75 to about 1.25 inches (about 1.91 to about 3.18 cm), and more preferably about 1 inch (about 2.54 cm). The length of the packed section 107 of the conduit 104 is typically from about 16 to about 50 inches (about 40.64 to about 127 cm), preferably from about 18.75 to about 37.5 inches (about 47.63 to about 95.25 cm), and more preferably about 25 inches (about 63.5 cm).

[0042] The shape of the conduit 104 can take various forms, and typically depends on the flow characteristics imparted by the shape, the compactness of the shape and/or the cost of manufacturing the conduit 104 with such a shape. Generally, a preferred conduit 104 has a compact shape and is relatively inexpensive to manufacture. For example, the

conduit 104 can comprise a linear or spiral tube. The conduit 104 preferably has a circular cross-sectional profile. In an alternative embodiment, the conduit 104 can have a cross-sectional profile of some other shape such as, for example, a non-circular ellipse.

[0043] The flow of the chemical to be purified contacts the purification material 105 disposed in the conduit 104, thereby reducing the amount of contaminant(s) present in the chemical. The contaminant(s) reduced typically depends at least on the type of purification material 105 that is employed. For example, in the case of hydrogen peroxide purification, at least one purification material can be employed that decreases the amount of an organic contaminant, an anionic contaminant, a cationic contaminant and/or combinations thereof, in the chemical to be purified.

[0044] The purification material 105 includes at least one type of material that is capable of purifying the chemical upon contact therewith. In a preferred embodiment, the purification material 105 comprises multiple types of purification material. The multiple types of purification material can be mixed to form a mixture, such as a homogeneous mixture, or the multiple types of purification material can be separately maintained in the conduit 104. For example, a material that allows the flow of the chemical therethrough but prevents the flow of the multiple types of purification material therethrough can be used to separate the multiple types of purification material. In a preferred embodiment, at least one separator such as, for example, a

screen, can be disposed in the cartridge 100 to separate the multiple types of purification material. It is noted however, that such a separator need not be employed, even where more than one purification material is used.

[0045] The purification material 105 can be periodically replaced to maintain the purification efficiency of the cartridge 100. The usable lifetime of the purification material 105 will depend on several factors including, for example, the type and/or amount of purification material 105 used, the dimensions of the cartridge 100, the purity of the chemical to be purified, and/or the flowrate of the chemical to be purified. For example, the useable lifetime of a mixture of DOWEX MONOSPHERE 550 CC NG OH anion resin and DOWEX MONOSPHERE C-650 NG H cation resin H form used for the purification of hydrogen peroxide was measured to be at least about 7000 BV (bed volumes). The usable lifetime of the purification material 105 preferably can be determined beforehand and the purification material 105 can be periodically replaced based on the predetermined usable lifetime. Alternatively, the purification material 105 can be replaced when the purity level of the purified chemical diminishes to a predetermined level.

[0046] The cartridge 100 is typically connected to a chemical source conduit to receive a flow of the chemical to be purified from a chemical source. The chemical source can include, for example, a bulk storage tank or a chemical delivery vehicle containing the chemical to be purified. The cartridge 100 is typically also connected to a product

conduit to remove the flow of the purified chemical therefrom. The product conduit can introduce the purified chemical to, for example, a storage tank or directly to a point of use, for example a semiconductor processing tool. Advantageously, the cartridge 100 can easily be disconnected from and connected to the chemical source conduit and the product conduit to replace the spent purification material 105, to replace cartridge 100, or for other maintenance purposes.

[0047] The cartridge 100 is preferably coaxially positioned with respect to the chemical source conduit and the product conduit. Such coaxial alignment typically imparts flow characteristics to the flow of chemical therethrough which are effective for increasing the purity level of the flow of the chemical therethrough. In a preferred embodiment, the diameter of the chemical source conduit is substantially equal to that of the inlet 102 of the cartridge 100. The diameter of the product conduit is preferably substantially equal to that of the outlet 106.

[0048] With reference again to FIG. 1A, the cartridge 100 typically includes a first end member 108 that can be attached to the inlet 102. A second end member 110 can be attached to the outlet 106. As will be described below, the first and second end members 108 and 110 can maintain the purification material 105 in the conduit 104. The first end member 108 can be connected to receive the flow of the chemical to be purified and provide the flow to the conduit 104, and the second end member 110 can be connected to

accommodate the flow of the purified chemical flowing out of the cartridge 100.

[0049] The end members 108 and 110 typically engage the inlet 102 and the outlet 106 of the conduit 104, respectively, to form liquid-tight seals therebetween. For example, the inlet 102 and outlet 106 can comprise flanges 140 and 142, respectively, into which the ends 144 and 146 of the end members 108 and 110 can be inserted, respectively.

[0050] The end members 108 and 110 can then be fastened to the conduit 104. For example, a first threaded portion 116 disposed on the first end member 108 can engage a second threaded portion 118 disposed on the inner surface of a first ring member 124. The first ring member 124 can be slideably and coaxially disposed about the conduit 104. The flange 140 of the inlet 102 can prevent the first ring member 124 from disengaging the conduit 104.

[0051] A third threaded portion 120 disposed on the second end member 110 can engage a fourth threaded portion 122 disposed on the inner surface of a second ring member 126. The second ring member 126 can be slideably and coaxially disposed about the conduit 104. The flange 142 of the outlet 106 can prevent the second ring member 126 from disengaging the conduit 104. Threaded portions that can be used include, for example, Flaretek and Purebond threaded fittings, and more preferably, 0.75 inch (1.91 cm) or 1 inch (2.54 cm) Flaretek and Purebond threaded fittings. Flaretek



fittings are available from Fluoroware. Purebond fittings are available from Fluoroware and George Fisher.

[0052] The first and second end members 108 and 110 can optionally include first and second screens 112 and 114. The screens 112 and 114 can retain the purification material 105 inside the conduit 104 while allowing the flow of the chemical to pass therethrough. The screens 112 and 114 can be formed of a material that is suitable for contacting the chemical to be purified such as, for example, high-density polyethylene. The end members 108 and 110 can be detached from the conduit 104, thereby providing access to the interior of the conduit 104 for various maintenance purposes, such as for replacing the purification material 105 and/or for cleaning the interior surface of the conduit 104.

[0053] Referring to FIG. 1B, which is an exploded view of the first end member 108, the screen 112 is typically disposed between first and second flanged portions 128 and 130. The first and second flanged portions 128 and 130 preferably engage to form a liquid-tight seal therebetween. The first and second flanged portions 128 and 130 can then be fastened together, for example, by engaging a fifth threaded portion 132 disposed on the first end member 108 with a sixth threaded portion 134 disposed on the inner surface of a third ring member 136. The third ring member 136 can be slideably and coaxially disposed about the first end member 108. Flaretek and Purebond fittings may be used to fasten the flanged portions 128 and 130 together. By

disengaging the first and second flanged portions 128 and 130, the screen 112 can be removed for various purposes such as, for example, replacing or cleaning the screen 112. The second end member 110 can have the same features as the first end member 108.

[0054] In an alternative embodiment, the screen 112 can be permanently positioned in the first end member 108. For example, referring to FIG. 1C, which is an exploded view of an alternative embodiment of the first end member 108, a commercially-available fitting, such as a Flaretek Union fitting, can be modified by milling the inner surface of an end of the fitting, thereby forming a milled end 150 of the first end member 108. A screen 112 can be positioned between the milled end 150 and an annular cap 152 and the annular cap 152 can be inserted into the milled end 150, thereby holding the screen 112 in place by friction fit, adhesive or other means. The screen 112 is preferably permanently positioned in the first end member 108 in this embodiment.

[0055] According to one aspect of the present invention, a detachable fitting for connection in a fluid transport line is provided. For example, according to one aspect of the present invention, the fitting can be an end member 108 and 110 described above. The fitting can easily be detached from the line, for example, to replace the fitting, to replace a device disposed in the fitting, or for other maintenance purposes. The fitting includes a conduit through which a flow of fluid may pass. The fitting can be

connected to and disconnected from a fluid-providing line and a fluid-removing line, preferably by using a connection device such as, for example, threading disposed on the outer surface of the conduit of the fitting.

[0056] The fitting includes a device which engages the flow of fluid passing through the fitting. For example, the device can include a screen, a membrane or a filter. The device is preferably removable from the conduit of the fitting.

[0057] The fitting is not limited to use in liquid purification systems. For example, the fitting can be used in any system which transports fluid and uses one of the devices described above. In a preferred embodiment, the fitting can include a filter and can be installed upstream from a pump. The fitting can also be used in a transport line that accommodates a gas flow.

[0058] Advantageously, the fitting and/or the device disposed therein can periodically be cleaned and/or replaced. For example, filters and membranes typically require periodic cleaning and/or replacement for efficient operation. The fitting is formed of a material that is compatible with the fluid that passes therethrough. Preferably, the fitting is formed of polytetrafluoroethylene, perfluoroalkoxy, polypropylene, polyvinyl difluoride or TEFLON®. Alternatively, the fitting can be formed of a metal.

[0059] The cartridge 100 can be formed of a material which is suitable for accommodating the chemical to be purified and the purification material 105. The cartridge 100 is preferably made of a flexible material that can expand when subjected to high pressure conditions. For example, according to a preferred embodiment, the cartridge 100 can withstand a pressure of at least about 110 psig without bursting, more preferably at least about 700 psig. The ability of the cartridge 100 to resist bursting will at least additionally depend on the wall thickness of the cartridge 100. Preferably, the cartridge 100 can be formed of a material such as, for example, perfluoroalkoxy (PFA), TEFLON® or the combination thereof, more preferably TEFLON®. These materials are generally more flexible than materials typically used in current chemical purification systems, such as, for example, polypropylene, polyvinylidene (PVDF) or the combination thereof. Alternatively, the cartridge 100 can be made of the more rigid materials set forth above.

[0060] The cartridge 100 is preferably operated under single-pass conditions, i.e., the flow of the chemical to be purified is preferably passed through the cartridge 100 only once. In an alternative embodiment of the present invention, part of or the entire flow of the purified chemical removed from the outlet 106 of the cartridge 100 can be introduced to the inlet 102 of the cartridge 100 for further purification.

[0061] The cartridge 100 can be arranged horizontally which provides more options for where the cartridge 100 can

be installed. Alternatively, the cartridge 100 can be arranged vertically or at an angle. In this alternative embodiment, the cartridge 100 is preferably positioned such that the chemical flows in an upward direction.

[0062] In a preferred embodiment, the cartridge 100 is used to purify a hydrogen peroxide solution. In such a case, the cartridge can contain one or more types of purification material. For example, a first type of purification material can be used which decreases the amount of an anionic contaminant, a second type can be used which decreases the amount of a cationic contaminant, and/or a third type can be used which decreases the amount of an organic contaminant, in the chemical to be purified. As stated above, if multiple types of purification materials are used, they can be mixed or separately maintained within the cartridge 100.

[0063] For reducing the presence of anionic contaminants in a hydrogen peroxide solution, the purification material preferably includes an anionic exchange resin such as, for example, DOWEX MONOSPHERE A550 UPN (polystyrene - DVB gel, quaternary ammonium, 1.0 eq.  $\text{OH}^-/\text{l}$ ) nuclear grade, available from Dow, or AMBERLITE IRA 958, available from Rohm and Haas (polyacrylic - DVB macroporous, quaternary ammonium 0.8 eq.  $\text{Cl}^-/\text{l}$ ). Other anionic resins that are known in the art can be used.

[0064] For reducing the amount of cationic contaminants in a hydrogen peroxide solution, the purification material

preferably includes a cationic exchange resin, such as, for example, DOWEX MONOSPHERE C650 UPN (polystyrene - DVB gel, sulfonic, 1.9 eq.  $H^+/l$ ), available from Dow, or IRA 963 available from Rohm and Haas. Other cationic exchange resins that are known in the art can be used.

[0065] The cationic and/or anionic exchange resins that can be used in the cartridge 100 are preferably preconditioned prior to use. For example, the anionic exchange resin is preferably preconditioned by initially loading the resin with bicarbonate ions. Bicarbonate preconditioning is described in, for example, U.S. Patent Nos. 3,294,488 and 3,305,314, the entire contents of which documents are hereby incorporated by reference. In general, bicarbonate preconditioning is preferred because other anions such as, for example, hydroxyl ( $OH^-$ ) and chloride ( $Cl^-$ ) ions, can catalyze the decomposition of hydrogen peroxide. The bicarbonate preconditioning step is preferably achieved by using a concentrated  $NH_4HCO_3$  solution. Alternatives to  $NH_4HCO_3$  can include, for example, an alkali bicarbonate, which typically requires removal of the alkali metal ions, or  $CO_2$ , the use of which is described in copending Application No. \_\_\_\_\_, Attorney Docket No. 016499-806, filed on even date herewith.

[0066] The cationic exchange resin is preferably preconditioned with an acid. For example, the cationic exchange resin can be preconditioned by contacting it with sulfuric acid, preferably a 10% molar solution of sulfuric acid.

[0067] An anionic/cationic resin mixture can optionally be used in place of or in addition to the anionic and/or cationic exchange resins. When a resin mixture is used in addition to the unmixed anionic and/or cationic exchange resins, the resin mixture is preferably disposed downstream from the unmixed anionic and/or cationic exchange resins.

[0068] A purification material for removing organic contaminants from the chemical to be purified can optionally be employed. Suitable materials for removing organic contaminants include, for example, AMBERLITE XAD-4 and AMBERSORB 563, available from Rohm and Haas. Other organic contaminant removal resins that are known in the art can be used.

[0069] The optional organic contaminant removal resin is preferably preconditioned. Preconditioning the resin typically reduces the content of metal impurities in the resin. Preferable techniques for preconditioning the organic contaminant removal resin are described in copending Application No. \_\_\_\_\_, Attorney Docket No. 016499-526, and Application No. \_\_\_\_\_, Attorney Docket No. 016499-650, filed on even date herewith, the entire contents of which applications are incorporated herein by reference.

[0070] For example, to precondition the organic contaminant removal resin, the resin can be rinsed with deionized water, preferably for from about 0.5 to 5 hours. The resin can then be contacted with an acid solution,

preferably for from about 3 to 8 hours. The acid solution is typically an aqueous solution of a strong acid such as, for example, hydrochloric acid, nitric acid or sulfuric acid. The acid-treated resin can then be rinsed with deionized water.

[0071] Additionally or alternatively, the resin can be rinsed with deionized water to remove various contaminants therefrom. Some contaminants are not completely removable by the deionized water such as, for example, chloride, boron, calcium, iron, magnesium, zinc, potassium, silicon and sodium. The presence of such contaminants can be reduced by contacting the resin with an effective amount of a preconditioning hydrogen peroxide solution. Advantageously, the preconditioning hydrogen peroxide solution can be conducted for at least 12 bed volumes (BV), with a hydrogen peroxide solution flow rate preferably of 0.1 to 0.6 BV/min.

[0072] The cartridge 100 of the present invention preferably reduces the contact time between the flow of the chemical and the purification material 105. Factors which contribute to this reduced contact time include, for example, the amount of the purification material 105 that is disposed in the conduit 104, the flow rate of the chemical through the conduit 104 and/or the flow characteristics of the flow of the chemical through the conduit 104. Preferably, the contact time between the flow of the chemical and the purification material 105 is sufficiently long to allow the chemical to be purified.



[0073] In the case of hydrogen peroxide purification, the reduced contact time between the hydrogen peroxide solution and the purification material 105 typically decreases the decomposition of the hydrogen peroxide solution, thereby decreasing the amount of oxygen gas produced therefrom. Also, the reduced contact time can decrease the amount of ionic contaminants such as, for example, sulfates and/or chlorides, that are typically released from the purification material 105 during periods of prolonged contact.

[0074] The flow rate of the chemical to be purified in the cartridge 100 should be set such that the desired flow characteristics and purification levels can be achieved. A typical flow rate is from about 0.05 to about 20 liters per minute (lpm), preferably from about 2 to about 5 lpm, more preferably about 3 lpm. This flow rate is preferably for a cartridge having a diameter of 1 inch (2.54 cm) and a length of 25 inches (68.5 cm).

[0075] The flow rate through the cartridge 100 preferably is maximized. While different flow characteristics may be desirable for different applications, a flow which is effective for reducing the contact time between the hydrogen peroxide solution and the purification material 105 is typically preferred for the purification of a hydrogen peroxide solution. Such a flow can provide several advantages including, for example, extending the lifetime of the purification material 105, and/or reducing the amount of

time required for the purified chemical to meet purity specifications during start up.

[0076] Referring to FIG. 2, according to another exemplary aspect of the present invention, an apparatus 200 for purifying a liquid chemical is provided. The apparatus 200 includes one or more of the cartridges 100 described above. For example, a plurality of the cartridges 100 can be employed, wherein the cartridges 100 are connected in series and/or in parallel. In a preferred embodiment, a plurality of cartridges 100 are connected in parallel.

[0077] More preferably, the apparatus 200 includes a plurality of groups of the cartridges 100, wherein each group includes at least two of the cartridges 100 connected in series. The plurality of groups of the cartridges 100 are preferably connected in parallel. The plurality of groups of the cartridges 100 can be arranged such that the flow of the chemical to be purified from the main inlet 201 is equally divided among the groups of the cartridges 100. The number of groups of the cartridges 100 depends, for example, on the desired flow rate of the purified chemical. By adjusting the number of groups of the cartridges 100 in the apparatus 200, the apparatus 200 can provide an amount of purified chemical comparable to that typically provided by current chemical purification systems.

[0078] In the case of hydrogen peroxide purification, each group of the cartridges 100 preferably includes three cartridges 100 connected in series. The first cartridge in

the series preferably contains an organic contaminant removal resin to decrease the amount of organic contaminants in the chemical to be purified. The second and third cartridges preferably are arranged downstream from the first cartridge and preferably contain an anionic exchange resin followed by a cationic exchange resin, or a cationic exchange resin followed by an anionic exchange resin. As described above, a single cartridge can optionally contain two or more of the purification materials. For example, a cartridge containing a mixture of anionic and cationic exchange resins can be arranged downstream from the cartridge containing the organic contaminant removal resin. The cartridge containing the organic contaminant removal resin can be eliminated when the hydrogen peroxide solution to be purified has a suitably low organic contaminant level.

[0079] Use of a plurality of groups of the cartridges 100 arranged in parallel allows for continuous purification. For example, a group of the cartridges 100 can be replaced without stopping flow to another group of the cartridges 100 arranged in parallel thereto. Maintaining an uninterrupted liquid chemical flow during cartridge replacement can be accomplished, for example, through manipulating valves V4, V7, V8, V11, V12 and/or V13. According to an exemplary embodiment, to replace the uppermost group of cartridges 100 in FIG. 2, normally opened valves V4 and V7 can be closed. Control devices that are known in the art can be used to facilitate the manipulation of the valves in the apparatus 200.

[0080] The apparatus 200 can include normally opened valves V1 and V3 which allow the chemical to be purified to flow into the apparatus 200 via the main inlet 201. At least one pump 220 can increase the pressure of the chemical to be purified that flows into the apparatus 200. The pump 220 can be, for example, a diaphragm pump such as the Yamada DP 20 diaphragm pump. A typical operating pressure in the apparatus 200 is from about 20 to about 70 psig, preferably about 35 psig.

[0081] The temperature of the chemical in the apparatus 200 will typically depend on the particular chemical. An optional heat exchanger 202 can be connected to heat or cool the incoming flow of the chemical to be purified. A typical operating temperature within the apparatus 200 is from about 20 to about 30°C, preferably about 25°C.

[0082] Normally opened valve V14 permits the purified chemical to be removed from the apparatus 200, for example, to be introduced to a storage container or directly to a point of use.

[0083] The apparatus 200 can optionally include a water inlet 204 and a water outlet 206 for passing a flow of water, preferably deionized water, through the apparatus 200. For example, water can be passed through the apparatus 200 for cleaning purposes. Valves V2 and V15, which are typically in the closed position, can be opened to introduce a flow of water to the apparatus 200 and to remove the flow therefrom, respectively. Normally opened valves V1 and V14

can be closed to prevent water from flowing into the source and/or product streams. Optional, normally-closed valves V5, V6, V9 and V10 can be opened when water is introduced into the apparatus 200.

[0084] The apparatus 200 can also include a controller 208 and a mass flow controller 212 for controlling the flow rate of the chemical to be purified into the apparatus 200. The controller 208 can be, for example, a programmable logic controller. A concentration analyzer 210 can be connected to measure the concentration of impurities present in the flow of the purified chemical after it has passed through the plurality of the cartridges 100. The controller 208 can manipulate the mass flow controller 212 to control the flow rate of the chemical based on the concentration of impurities in the purified chemical measured by the concentration analyzer 210. For example, the presence of certain ions in the product stream can be reduced by adjusting the flow rate of the chemical. A display 209 can provide the user with various information regarding the status of the apparatus 200.

[0085] Safety features such as safety interlocks and safety valves are typically not required in the apparatus 200 because the plurality of the cartridges 100 can withstand high pressures and temperatures without bursting. Costs of implementing and maintaining such features, which are typically used in conventional columns, can thereby be avoided.

[0086] Alternatively, the apparatus 200 can optionally include pressure valves V17, V18, V19 and/or V20 which open to relieve pressure in the apparatus 200, for example, when the pressure in the apparatus 200 reaches a first predetermined value. The first predetermined value can be based on several factors including, for example, the number of cartridges 100 in the apparatus 200, the type of material the cartridges 100 are made of and/or the type of chemical being purified. For example, the first predetermined value can be set at about 100 psig. Typically, the first predetermined value is lower than the pressure at which the cartridge 100 is expected to burst.

[0087] In the event of overpressurization inside the apparatus 200, i.e., when the first predetermined value is reached, the pressure valves V17, V18, V19 and/or V20 can be opened until the pressure returns to a second predetermined value, at which point the valves V17, V18, V19 and/or V20 can be closed. The valves V17, V18, V19 and/or V20 preferably automatically open when the first predetermined value is reached. The second predetermined value can be the normal operating pressure of the apparatus 200, such as, for example, 35 psig. The chemical that is removed during the depressurization of the apparatus 200 can be purged by opening normally closed valve V16.

[0088] The apparatus 200 can be housed in an enclosure that provides convenient access for the periodic replacement of the cartridges 100. The enclosure is preferably formed

of a material compatible with the chemicals being treated, in the event of leakage.

[0089] The apparatus 200 of the present invention can be located on-site in a facility, for example, a semiconductor fabrication facility, or proximate to the facility. For example, referring to FIG. 3, the apparatus 200 can be located outside a facility 400 in which the purified chemical is used. The apparatus 200 can be connected to receive the chemical to be purified from a mobile source 300 such as, for example, a tube trailer. The apparatus 200 can provide the purified chemical to a storage tank 500, and the purified chemical can then be transported using pump P1 to the facility 400. In this example, the flow rate of the chemical into the apparatus 200 is typically relatively high to quickly unload the chemical from the mobile source 300.

[0090] Referring to FIG. 4, according to another exemplary embodiment, the chemical can be unloaded from a mobile source 300 to a storage tank 500. The apparatus 200, which is located within the facility 400, can be connected to receive the chemical from the storage tank 500 and to pass the purified chemical to a day tank 402.

[0091] Referring to FIG. 5, according to another exemplary embodiment, the apparatus 200 can be connected to receive the chemical from a CDU 600 which receives the chemical from a day tank 402. The apparatus 200 can then send the purified chemical to various points of use 404 such as, for example, one or more semiconductor processing tools.

[0092] Referring to FIG. 6, according to a further exemplary embodiment, the apparatus 200 can be connected to receive the chemical from a bulk storage tank 700. The apparatus 200 can provide the purified chemical to a plurality of intermediate storage tanks 800. The purified product can then be passed to a quality control station 802, wherefrom the product can be distributed to various facilities such as, for example, a CDU 600, a mobile chemical vessel (MCV) fill 804 or a drum fill 806. The drum is typically a cylindrical container, preferably having a volume of about 55 gallons.

[0093] The apparatus 200 of the present invention can be relatively compact in size compared to current chemical purification systems. As a result, the present apparatus 200 can be placed in areas which typically cannot accommodate a chemical purification system. For example, the apparatus 200 can be attached to a wall of a building, similar to a valve manifold box (VMB), or be attached to a CDU, similar to a filter assembly. The apparatus 200 can also be installed on a chemical delivery vehicle.

[0094] In order to further illustrate the present invention and the advantages thereof, the following specific examples are given, it being understood that the examples are intended only as illustrative and are in no way limiting.



EXAMPLES

EXAMPLE 1: PURIFICATION OF A HYDROGEN PEROXIDE SOLUTION

[0095] A cartridge as described above and as illustrated in FIG. 1A was used to purify a flow of a hydrogen peroxide solution. The cartridge was formed of PFA. The inside diameter of the cartridge was 0.87 inch (2.22 cm), and the outside diameter was 1 inch (2.54 cm). The length of the packed section was 25 inches (63.5 cm). The cross-sectional area of the conduit was 3.88 cm<sup>2</sup> and the resin bed volume (BV) was 246 cc. The purification material present in the cartridge was a mixture of DOWEX MONOSPHERE 550 LC NG OH anion resin and DOWEX MONOSPHERE C-650 NG H cation resin H form, available from Dow.

[0096] A flow of a hydrogen peroxide solution was passed through the cartridge at a constant flow rate of 1.6 liters per minute (6.5 BV per minute). The pressure drop across the cartridge was 2.5 bar (250 kPa).

[0097] The concentrations (in ppb) of various contaminants in the hydrogen peroxide solution were measured after 0 (0 BV), 10 (64 BV), 30 (192 BV), 60 (384 BV), 90 (576 BV) and 120 (768 BV) minutes of passing the flow of the hydrogen peroxide solution through the cartridge. The results are shown in Table 1.

[0098] As can be seen from Table 1, the cartridge provided a purified hydrogen peroxide solution with significantly reduced levels of many contaminants at each measured interval, particularly at the 120 minute interval.

For example, the amount of chloride ions was conspicuously reduced from 26 ppb to 7 ppb at 120 minutes. Also, the amount of sulfate ions was reduced from 34 ppb to 2 ppb at 120 minutes. In comparison, a purification column having an inside diameter of 4 inches and a resin column length of 25 inches provided a hydrogen peroxide solution having an optimized nitrate concentration of 14 ppb and an optimized sulfate concentration of 16 ppb.

**TABLE 1**

	0	10	30	60	90	120
Bromide	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Chloride	26.0	<0.5	16.0	3.0	4.0	7.0
Nitrate	9.0	8.0	9.0	10.0	9.0	8.0
Nitrite	1.0	13.0	<0.5	2.0	2.0	2.0
Phosphate	<1.0	8.0	<1.0	<1.0	<1.0	<1.0
Sulfate	35.0	24.0	17.0	3.0	2.0	2.0
Calcium	0.260	0.010	0.010	<0.010	<0.010	<0.010
Iron	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
Potassium	0.020	<0.010	<0.010	<0.010	<0.010	<0.010
Sodium	0.490	0.050	0.030	0.020	0.030	0.030
Aluminum	0.190	0.030	<0.010	<0.010	<0.010	0.010
Antimony	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Arsenic	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Barium	0.080	0.020	<0.010	<0.010	<0.010	<0.010
Beryllium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Bismuth	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Boron	0.890	<0.010	0.010	<0.010	<0.010	<0.010
Cadmium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Chromium	<0.120	<1.720	<0.470	<0.230	<0.230	<0.190
Cobalt	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Copper	0.020	<0.010	<0.010	<0.010	<0.010	<0.010
Gallium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Germanium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010

	0	10	30	60	90	120
Gold	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Indium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Lanthanum	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Lead	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Lithium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Magnesium	0.280	0.070	<0.010	<0.010	<0.010	<0.010
Manganese	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Molybdenum	0.010	0.450	<0.010	<0.010	<0.010	<0.010
Nickel	0.050	0.030	<0.010	<0.010	<0.010	<0.010
Niobium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Palladium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Platinum	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Silver	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Strontium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Tantalum	<0.070	<0.040	<0.150	<0.020	<0.010	<0.030
Thallium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Tin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Titanium	0.050	0.020	0.020	<0.010	0.010	0.030
Tungsten	<0.010	<0.010	<0.010	<0.010	<0.010	0.010
Vanadium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Zinc	0.270	0.090	0.020	<0.010	<0.010	0.020
Zirconium	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010

[0099] The measured useable lifetime of the purification material was at least about 18 hours (7000 BV). Referring to Table 2, hydrogen peroxide was further introduced to the cartridge and the concentrations of various cations were measured up to 13628 BV.

TABLE 2

BV	Fe	K	Na	Ca	B	Mg	Ni	Zn
960	<0.050	<0.010	0.06	0.01	0.01	0.07	0.01	0.01
1008	<0.050	<0.010	0.03	0.01	0.01	0.01	0.01	0.01
1248	<0.050	<0.010	0.03	0.01	0.01	0.01	0.01	0.01
1488	<0.050	<0.010	0.04	0.01	0.01	0.01	0.01	0.01
1728	<0.050	<0.010	0.04	0.01	0.01	0.01	0.01	0.01
1968	<0.050	<0.010	0.04	0.03	0.01	0.01	0.01	0.02
4788	<0.050	<0.010	0.03	0.01	0.01	0.01	0.01	0.03
4908	<0.050	<0.010	0.02	0.01	0.01	0.01	0.01	0.1
5148	<0.050	<0.010	0.01	0.01	0.01	0.01	0.01	0.1
5388	<0.050	<0.010	0.01	0.01	0.01	0.01	0.01	0.1
5628	<0.050	<0.010	0.02	0.01	0.01	0.01	0.01	0.02
6028	<0.050	<0.010	0.02	0.01	0.02	0.06	0.01	0.01
6428	<0.050	<0.010	0.02	0.01	0.01	0.08	0.01	0.01
6828	<0.050	<0.010	0.02	0.01	0.01	0.13	0.01	0.01
7228	<0.050	<0.010	0.02	0.01	0.05	0.01	0.01	0.01
7628	<0.050	<0.010	0.02	0.01	0.04	0.01	0.01	0.01
8028	<0.050	<0.010	0.01	0.01	0.06	0.01	0.01	0.01
8428	<0.050	<0.010	0.02	0.02	0.04	0.01	0.03	0.02
8828	<0.050	<0.010	0.02	0.01	0.04	0.01	0.02	0.03
9228	<0.050	<0.010	0.03	0.01	0.05	0.01	0.01	0.02
9628	<0.050	<0.010	0.01	0.02	0.05	0.01	0.01	0.03
10028	<0.050	<0.010	0.04	0.01	0.06	0.01	0.02	0.02
10428	<0.050	<0.010	0.03	0.01	0.1	0.01	0.02	0.02
10828	<0.050	<0.010	0.03	0.01	0.09	0.01	0.02	0.02
11228	<0.050	<0.010	0.02	0.01	0.14	0.01	0.01	0.01
11628	<0.050	<0.010	0.02	0.01	0.12	0.01	0.01	0.01
12028	<0.050	<0.010	0.01	0.01	0.12	0.01	0.01	0.01
12428	<0.050	<0.010	0.02	0.01	0.09	0.01	0.01	0.01
12828	<0.050	<0.010	0.02	0.01	0.12	0.01	0.01	0.01

BV	Fe	K	Na	Ca	B	Mg	Ni	Zn
13228	<0.050	<0.010	0.02	0.01	0.11	0.01	0.02	0.01
13628	<0.050	<0.010	0.02	0.02	0.09	0.01	0.05	0.01

[00100] The purification material in the cartridge became no longer useable when a breakthrough of ionic contaminants was detected, for example, Boron, Aluminum and/or Nickel typically are the first ionic contaminants to increase in concentration.

#### EXAMPLE 2: EXERTING INTERNAL PRESSURE USING WATER

[00101] A cartridge made of PFA withstood a high internal pressure for several days without bursting. In this example, water was introduced to a PFA cartridge to determine the amount of pressure the cartridge could withstand. The cartridge did not burst until being subjected to a pressure of about 650 to about 700 psig. In addition, the breach of the cartridge did not release a large amount of liquid.

#### EXAMPLE 3: EXERTING INTERNAL PRESSURE USING A HYDROGEN PEROXIDE SOLUTION

[00102] A hydrogen peroxide solution was introduced to a PFA cartridge to determine the amount of pressure the cartridge could withstand. The cartridge withstood about 100 psig of pressure without bursting. In this example, oxygen gas formed from the decomposition of the hydrogen peroxide solution increased the internal pressure of the cartridge.

[00103] While the invention has been described in detail with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made, and equivalents employed without departing from the scope of the claims.

11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102  
103  
104  
105  
106  
107  
108  
109  
110  
111  
112  
113  
114  
115  
116  
117  
118  
119  
120  
121  
122  
123  
124  
125  
126  
127  
128  
129  
130  
131  
132  
133  
134  
135  
136  
137  
138  
139  
140  
141  
142  
143  
144  
145  
146  
147  
148  
149  
150  
151  
152  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163  
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201  
202  
203  
204  
205  
206  
207  
208  
209  
210  
211  
212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226  
227  
228  
229  
230  
231  
232  
233  
234  
235  
236  
237  
238  
239  
240  
241  
242  
243  
244  
245  
246  
247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267  
268  
269  
270  
271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322  
323  
324  
325  
326  
327  
328  
329  
330  
331  
332  
333  
334  
335  
336  
337  
338  
339  
340  
341  
342  
343  
344  
345  
346  
347  
348  
349  
350  
351  
352  
353  
354  
355  
356  
357  
358  
359  
360  
361  
362  
363  
364  
365  
366  
367  
368  
369  
370  
371  
372  
373  
374  
375  
376  
377  
378  
379  
380  
381  
382  
383  
384  
385  
386  
387  
388  
389  
390  
391  
392  
393  
394  
395  
396  
397  
398  
399  
400  
401  
402  
403  
404  
405  
406  
407  
408  
409  
410  
411  
412  
413  
414  
415  
416  
417  
418  
419  
420  
421  
422  
423  
424  
425  
426  
427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444  
445  
446  
447  
448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468  
469  
470  
471  
472  
473  
474  
475  
476  
477  
478  
479  
480  
481  
482  
483  
484  
485  
486  
487  
488  
489  
490  
491  
492  
493  
494  
495  
496  
497  
498  
499  
500  
501  
502  
503  
504  
505  
506  
507  
508  
509  
510  
511  
512  
513  
514  
515  
516  
517  
518  
519  
520  
521  
522  
523  
524  
525  
526  
527  
528  
529  
530  
531  
532  
533  
534  
535  
536  
537  
538  
539  
540  
541  
542  
543  
544  
545  
546  
547  
548  
549  
550  
551  
552  
553  
554  
555  
556  
557  
558  
559  
560  
561  
562  
563  
564  
565  
566  
567  
568  
569  
570  
571  
572  
573  
574  
575  
576  
577  
578  
579  
580  
581  
582  
583  
584  
585  
586  
587  
588  
589  
590  
591  
592  
593  
594  
595  
596  
597  
598  
599  
600  
601  
602  
603  
604  
605  
606  
607  
608  
609  
610  
611  
612  
613  
614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644  
645  
646  
647  
648  
649  
650  
651  
652  
653  
654  
655  
656  
657  
658  
659  
660  
661  
662  
663  
664  
665  
666  
667  
668  
669  
670  
671  
672  
673  
674  
675  
676  
677  
678  
679  
680  
681  
682  
683  
684  
685  
686  
687  
688  
689  
690  
691  
692  
693  
694  
695  
696  
697  
698  
699  
700  
701  
702  
703  
704  
705  
706  
707  
708  
709  
710  
711  
712  
713  
714  
715  
716  
717  
718  
719  
720  
721  
722  
723  
724  
725  
726  
727  
728  
729  
730  
731  
732  
733  
734  
735  
736  
737  
738  
739  
740  
741  
742  
743  
744  
745  
746  
747  
748  
749  
750  
751  
752  
753  
754  
755  
756  
757  
758  
759  
760  
761  
762  
763  
764  
765  
766  
767  
768  
769  
770  
771  
772  
773  
774  
775  
776  
777  
778  
779  
780  
781  
782  
783  
784  
785  
786  
787  
788  
789  
790  
791  
792  
793  
794  
795  
796  
797  
798  
799  
800  
801  
802  
803  
804  
805  
806  
807  
808  
809  
810  
811  
812  
813  
814  
815  
816  
817  
818  
819  
820  
821  
822  
823  
824  
825  
826  
827  
828  
829  
830  
831  
832  
833  
834  
835  
836  
837  
838  
839  
840  
841  
842  
843  
844  
845  
846  
847  
848  
849  
850  
851  
852  
853  
854  
855  
856  
857  
858  
859  
860  
861  
862  
863  
864  
865  
866  
867  
868  
869  
870  
871  
872  
873  
874  
875  
876  
877  
878  
879  
880  
881  
882  
883  
884  
885  
886  
887  
888  
889  
890  
891  
892  
893  
894  
895  
896  
897  
898  
899  
900  
901  
902  
903  
904  
905  
906  
907  
908  
909  
910  
911  
912  
913  
914  
915  
916  
917  
918  
919  
920  
921  
922  
923  
924  
925  
926  
927  
928  
929  
930  
931  
932  
933  
934  
935  
936  
937  
938  
939  
940  
941  
942  
943  
944  
945  
946  
947  
948  
949  
950  
951  
952  
953  
954  
955  
956  
957  
958  
959  
960  
961  
962  
963  
964  
965  
966  
967  
968  
969  
970  
971  
972  
973  
974  
975  
976  
977  
978  
979  
980  
981  
982  
983  
984  
985  
986  
987  
988  
989  
990  
991  
992  
993  
994  
995  
996  
997  
998  
999  
1000  
1001  
1002  
1003  
1004  
1005  
1006  
1007  
1008  
1009  
1010  
1011  
1012  
1013  
1014  
1015  
1016  
1017  
1018  
1019  
1020  
1021  
1022  
1023  
1024  
1025  
1026  
1027  
1028  
1029  
1030  
1031  
1032  
1033  
1034  
1035  
1036  
1037  
1038  
1039  
1040  
1041  
1042  
1043  
1044  
1045  
1046  
1047  
1048  
1049  
1050  
1051  
1052  
1053  
1054  
1055  
1056  
1057  
1058  
1059  
1060  
1061  
1062  
1063  
1064  
1065  
1066  
1067  
1068  
1069  
1070  
1071  
1072  
1073  
1074  
1075  
1076  
1077  
1078  
1079  
1080  
1081  
1082  
1083  
1084  
1085  
1086  
1087  
1088  
1089  
1090  
1091  
1092  
1093  
1094  
1095  
1096  
1097  
1098  
1099  
1100  
1101  
1102  
1103  
1104  
1105  
1106  
1107  
1108  
1109  
1110  
1111  
1112  
1113  
1114  
1115  
1116  
1117  
1118  
1119  
1120  
1121  
1122  
1123  
1124  
1125  
1126  
1127  
1128  
1129  
1130  
1131  
1132  
1133  
1134  
1135  
1136  
1137  
1138  
1139  
1140  
1141  
1142  
1143  
1144  
1145  
1146  
1147  
1148  
1149  
1150  
1151  
1152  
1153  
1154  
1155  
1156  
1157  
1158  
1159  
1160  
1161  
1162  
1163  
1164  
1165  
1166  
1167  
1168  
1169  
1170  
1171  
1172  
1173  
1174  
1175  
1176  
1177  
1178  
1179  
1180  
1181  
1182  
1183  
1184  
1185  
1186  
1187  
1188  
1189  
1190  
1191  
1192  
1193  
1194  
1195  
1196  
1197  
1198  
1199  
1200  
1201  
1202  
1203  
1204  
1205  
1206  
1207  
1208  
1209  
1210  
1211  
1212  
1213  
1214  
1215  
1216  
1217  
1218  
1219  
1220  
1221  
1222  
1223  
1224  
1225  
1226  
1227  
1228  
1229  
1230  
1231  
1232  
1233  
1234  
1235  
1236  
1237  
1238  
1239  
1240  
1241  
1242  
1243  
1244  
1245  
1246  
1247  
1248  
1249  
1250  
1251  
1252  
1253  
1254  
1255  
1256  
1257  
1258  
1259  
1260  
1261  
1262  
1263  
1264  
1265  
1266  
1267  
1268  
1269  
1270  
1271  
1272  
1273  
1274  
1275  
1276  
1277  
1278  
1279  
1280  
1281  
1282  
1283  
1284  
1285  
1286  
1287  
1288  
1289  
1290  
1291  
1292  
1293  
1294  
1295  
1296  
1297  
1298  
1299  
1300  
1301  
1302  
1303  
1304  
1305  
1306  
1307  
1308  
1309  
1310  
1311  
1312  
1313  
1314  
1315  
1316  
1317  
1318  
1319  
1320  
1321  
1322  
1323  
1324  
1325  
1326  
1327  
1328  
1329  
1330  
1331  
1332  
1333  
1334  
1335  
1336  
1337  
1338  
1339  
1340  
1341  
1342  
1343  
1344  
1345  
1346  
1347  
1348  
1349  
1350  
1351  
1352  
1353  
1354  
1355  
1356  
1357  
1358  
1359  
1360  
1361  
1362  
1363  
1364  
1365  
1366  
1367  
1368  
1369  
1370  
1371  
1372  
1373  
1374  
1375  
1376  
1377  
1378  
1379  
1380  
1381  
1382  
1383  
1384  
1385  
1386  
1387  
1388  
1389  
1390  
1391  
1392  
1393  
1394  
1395  
1396  
1397  
1398  
1399  
1400  
1401  
1402  
1403  
1404  
1405  
1406  
1407  
1408  
1409  
1410  
1411  
1412  
1413  
1414  
1415  
1416  
1417  
1418  
1419  
1420  
1421  
1422  
1423  
1424  
1425  
1426  
1427  
1428  
1429  
1430  
1431  
1432  
1433  
1434  
1435  
1436  
1437  
1438  
1439  
1440  
1441  
1442  
1443  
1444  
1445  
1446  
1447  
1448  
1449  
1450  
1451  
1452  
1453  
1454  
1455  
1456  
1457  
1458  
1459  
1460  
1461  
1462  
1463  
1464  
1465  
1466  
1467  
1468  
1469  
1470  
1471  
1472  
1473  
1474  
1475  
1476  
1477  
1478  
1479  
1480  
1481  
1482  
1483  
1484  
1485  
1486  
1487  
1488  
1489  
1490  
1491  
1492  
1493  
1494  
1495  
1496  
1497  
1498  
1499  
1500  
1501  
1502  
1503  
1504  
1505  
1506  
1507  
1508  
1509  
1510  
1511  
1512  
1513  
1514  
1515  
1516  
1517  
1518  
1519  
1520  
1521  
1522  
1523  
1524  
1525  
1526  
1527  
1528  
1529  
1530  
1531  
1532  
1533  
1534  
1535  
1536  
1537  
1538  
1539  
1540  
1541  
1542  
1543  
1544  
1545  
1546  
1547  
1548  
1549  
1550  
1551  
1552  
1553  
1554  
1555  
1556  
1557  
1558  
1559  
1560  
1561  
1562  
1563  
1564  
1565  
1566  
1567  
1568  
1569  
1570  
1571  
1572  
1573  
1574  
1575  
1576  
1577  
1578  
1579  
1580  
1581  
1582  
1583  
1584  
1585  
1586  
1587  
1588  
1589  
1590  
1591  
1592  
1593  
1594  
1595  
1596  
1597  
1598  
1599  
1600  
1601  
1602  
1603  
1604  
1605  
1606  
1607  
1608  
1609  
1610  
1611  
1612  
1613  
1614  
1615  
1616  
1617  
1618  
1619  
1620  
1621  
1622  
1623  
1624  
1625  
1626  
1627  
1628  
1629  
1630  
1631  
1632  
1633  
1634  
1635  
1636  
1637  
1638  
1639  
1640  
1641  
1642  
1643  
1644  
1645  
1646  
1647  
1648  
1649  
1650  
1651  
1652  
1653  
1654  
1655  
1656  
1657  
1658  
1659  
1660  
1661  
1662  
1663  
1664  
1665  
1666  
1667  
1668  
1669  
1670  
1671  
1672  
1673  
1674  
1675  
1676  
1677  
1678  
1679  
1680  
1681  
1682  
1683  
1684  
1685  
1686  
1687  
1688  
1689  
1690  
1691  
1692  
1693  
1694  
1695  
1696  
1697  
1698  
1699  
1700  
1701  
1702  
1703  
1704  
1705  
1706  
1707  
1708  
1709  
1710  
1711  
1712  
1713  
1714  
1715  
1716  
1717  
1718  
1719  
1720  
1721  
1722  
1723  
1724  
1725  
1726  
1727  
1728  
1729  
1730  
1731  
1732  
1733  
1734  
1735  
1736  
1737  
1738  
1739  
1740  
1741  
1742  
1743  
1744  
1745  
1746  
1747  
1748  
1749  
1750  
1751  
1752  
1753  
1754  
1755  
1756  
1757  
1758  
1759  
1760  
1761  
1762  
1763  
1764  
1765  
1766  
1767  
1768  
1769  
1770  
1771  
1772  
1773  
1774  
1775  
1776  
1777  
1778  
1779  
1780  
1781  
1782  
1783  
1784  
1785  
1786  
1787  
1788  
1789  
1790  
1791  
1792  
1793  
1794  
1795  
1796  
1797  
1798  
1799  
1800  
1801  
1802  
1803  
1804  
1805  
1806  
1807  
1808  
1809  
1810  
1811  
1812  
1813  
1814  
1815  
1816  
1817  
1818  
1819  
1820  
1821  
1822  
1823  
1824  
1825  
1826  
1827  
1828  
1829  
1830  
1831  
1832  
1833  
1834  
1835  
1836  
1837  
1838  
1839  
1840  
1841  
1842  
1843  
1844  
1845  
1846  
1847  
1848  
1849  
1850  
1851  
1852  
1853  
1854  
1855  
1856  
1857  
1858  
1859  
1860  
1861  
1862  
1863  
1864  
1865  
1866  
1867  
1868  
1869  
1870  
1871  
1872  
1873  
1874  
1875  
1876  
1877  
1878  
1879  
1880  
1881  
1882  
1883  
1884  
1885  
1886  
1887  
1888  
1889  
1890  
1891  
1892  
1893  
1894  
1895  
1896  
1897  
1898  
1899  
1900  
1901  
1902  
1903  
1904  
1905  
1906  
1907  
1908  
1909  
1910  
1911  
1912  
1913  
1914  
1915  
1916  
1917  
1918  
1919  
1920  
1921  
1922  
1923  
1924  
1925  
1926  
1927  
1928  
1929  
1930  
1931  
1932  
1933  
1934  
1935  
1936  
1937  
1938  
1939  
1940  
1941  
1942  
1943  
1944  
1945  
1946  
1947  
1948  
1949  
1950  
1951  
1952  
1953  
1954  
1955  
1956  
1957  
1958  
1959  
1960  
1961  
1962  
1963  
1964  
1965  
1966  
1967  
1968  
1969  
1970  
1971  
1972  
1973  
1974  
1975  
1976  
1977  
1978  
1979  
1980  
1981  
1982  
1983  
1984  
1985  
1986  
1987  
1988  
1989  
1990  
1991  
1992  
1993  
1994  
1995  
1996  
1997  
1998  
1999  
2000  
2001  
2002  
2003  
2004  
2005  
2006  
2007  
2008  
2009  
2010  
2011  
2012  
2013  
2014  
2015  
2016  
2017  
2018  
2019  
2020  
2021  
2022  
2023  
2024  
2025  
2026  
2027  
2028  
2029  
2030  
2031  
2032  
2033  
2034  
2035  
2036  
2037  
2038  
2039  
2040  
2041  
2042  
2043  
2044  
2045  
2046  
2047  
2048  
2049  
2050  
2051  
2052  
2053  
2054  
2055  
2056  
2057  
2058  
2059  
2060  
2061  
2062  
2063  
2064  
2065  
2066  
2067  
2068  
2069  
2070  
2071  
2072  
2073  
2074  
2075  
2076  
2077  
2078  
2079  
2080  
2081  
2082  
2083  
2084  
2085  
2086  
2087  
2088  
2089  
2090  
2091  
2092  
2093  
2094  
2095  
2096  
2097  
2098  
2099  
2100  
2101  
2102  
2103  
2104  
2105  
2106  
2107  
2108  
2109  
2110  
2111  
2112  
2113  
2114  
2115  
2116  
2117  
2118  
2119  
2120  
2121  
2122  
2123  
2124  
2125  
2126  
2127  
2128  
2129  
2130  
2131  
2132  
2133  
2134  
2135  
2136  
2137  
2138  
2139  
2140  
2141  
2142  
2143  
2144  
2145  
2146  
2147  
2148  
2149  
2150  
2151  
2152  
2153  
2154  
2155  
2156  
2157  
2158  
2159  
2160  
2161  
2162  
2163  
2164  
2165  
2166  
2167  
2168  
2169  
2170  
2171  
2172  
2173  
2174  
2175  
2176  
2177  
2178  
2179  
2180  
2181  
2182  
2183  
2184  
2185  
2186  
2187  
2188  
2189  
2190  
2191  
2192  
2193  
2194  
2195  
2196  
2197  
2198  
2199  
2200  
2201  
2202  
2203  
2204  
2205  
2206  
2207  
2208  
2209  
2210  
2211  
2212  
2213  
2214  
2215  
2216  
2217  
2218  
2219  
2220  
2221  
2222  
2223  
2224  
2225  
2226  
2227  
2228  
2229  
2